Theoretical Studies of Carbon-hydrogen Bond Activation Chemistry of Actinide Complexes

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The thorium(IV) and uranium(IV) alkyl complexes $(C_5Me_5)_2AnR_2$ (where An = Th, U; R = CH_3, CPh, Ph) have proven to be versatile starting materials for the synthesis of a diverse array of actinide organometallic systems containing An-N bonds such as imido, hydrazonato, and ketimido complexes, which feature novel electronic properties [1]. Recently, the Kiplinger group at Los Alamos National Laboraotry in MPA-10 reported that these actinide alkyl complexes undergo interesting C-H and C-N bond cleavage chemistry with N-heterocycles [2] such as 2-picoline (2-methylpyridine), which possesses both sp^2 and sp^3 hybridized C-H bonds. The thorium alkyl complex $(C_5Me_5)_2Th(CH_3)_2$ activates both the sp^3 C-H bond on the 2-picoline methyl group and the *ortho* sp^2 C-H bond on the ring. This is in marked contrast to the uranium system, which only reacts with a sp^2 C-H bond on the 2-picoline aromatic ring (Fig. 1). Deuterium labeling studies demonstrated that the thorium and uranium $(C_5Me_5)_2An(CH_3)_2$ complexes react with 2-picoline by different mechanistic reaction pathways.

Density functional theory (DFT) methods have been employed to explore actinide-ligand interactions, such as structures, thermochemistry, and spectroscopic properties, using hybrid functionals [3,4]. We have performed a computational study of the competitive sp^2 versus sp^3 C-H activations. The products and resulting thermochemistry in these reactions are compared, and likely reaction precursors and transition states are also identified, as well the plausible reaction pathways.

The results of theoretical study are consistent with reported experimental results. Optimized geometries are in excellent agreement with X-ray crystal data. The calculated reaction energies prove that the sp^2 C-H bond activation product is the most stable structure (i.e., thermodynamic) product. Both theoretical and experimental observations point to the sp^3 product as the kinetic product and the sp^2 product as the thermodynamic product for thorium, while the sp^2 product is both the kinetic and thermodynamic selection in the uranium scheme (Fig. 1). The reaction initiates from formation of a weakly bound adduct, followed by the activation of adjacent C–H activation by An-center leading to an agostic transition state. We find that the actinide atom plays a fundamental role during the hydrogen migration process from 2-picoline to the methyl leaving group. Agostic 5-centered transition structures for the actinide C–H activation reaction pathways have not been reported before, to the best of our knowledge. The origin of the regioselectivity of these reactions rests in these highly ordered configurations of transition states. Despite many common features found between thorium and uranium systems, including the similar geometries of products, adducts and the agostic transition states, the relative activation energies between sp^2 and sp^3 activation differ slightly:

$$\text{Th: } \Delta E^{\neq}_{sp^3} < \Delta E^{\neq}_{sp^2} \qquad \text{U: } \Delta E^{\neq}_{sp^2} < \Delta E^{\neq}_{sp^3}$$

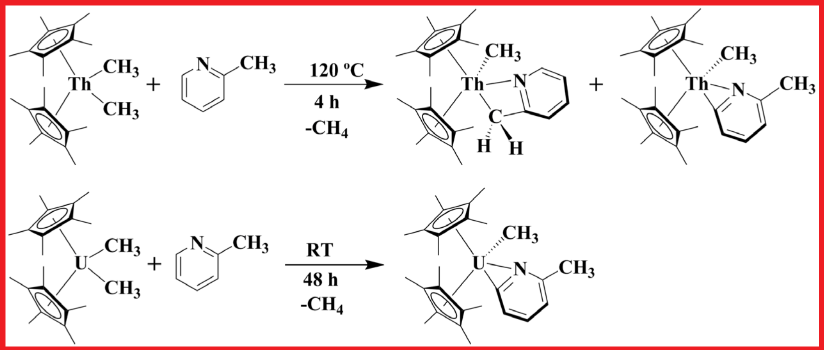
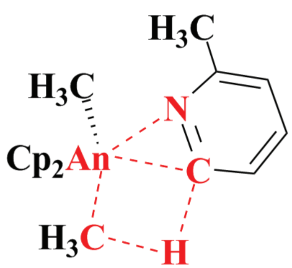
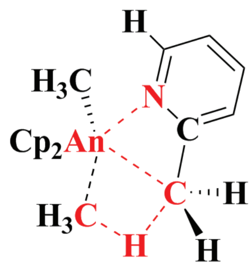
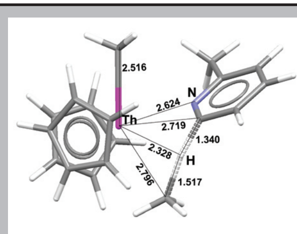
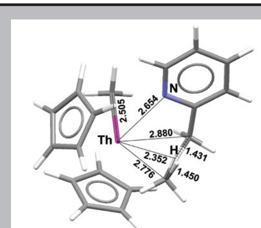
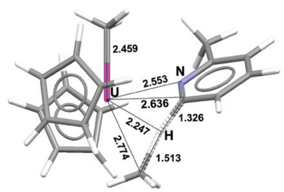
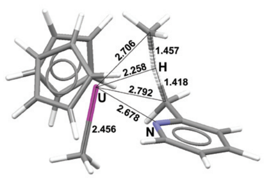


Fig. 1. The thorium alkyl complex $(C_5Me_5)_2Th(CH_3)_2$ and 2-picoline react to give preferential sp^3 C-H bond activation in the presence of a more reactive sp^2 C-H bond, while the analogous uranium complex, $(C_5Me_5)_2U(CH_3)_2$, reacts with only the ortho 2-picoline sp^2 C-H bond.

On the basis of the combination of labeling, structural, and computational information, we proposed a general mechanism for the C–H activation of N-heterocycle by actinocene complexes. “Agostic migration” cyclomelatation is indicated as an operative mechanism.

Table 1: The calculated 3D structures of the transition states involved in the sp^2 and sp^3 C-H bond activation of 2-picoline from the most stable thorium and uranium adducts.

	sp^2 activation	sp^3 activation
Complex		
Thorium		
Uranium		

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